

Fluorinated Siloxane Amine Oligomers

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ABSTRACT: Fluorine-containing siloxane oligomers were made from bis(aminopropyl)tetramethyldisiloxane and trimethyltris(trifluoropropyl)cyclotrisiloxane. These materials were characterized by IR spectroscopy, size exclusion chromatography, nonaqueous colorimetric end group titration, and ^1H -NMR. The end groups of one oligomer were chemically modified for an increased NMR signal for molecular weight determination. The cyclic trimeric siloxane starting material was additionally studied via ^{13}C -, ^{29}Si -, and ^{19}F -NMR. Two forms of it were used: a white solid obtained at room temperature, and a colorless liquid isolated at low temperature. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 1315–1320, 2000

Key words: fluorinated siloxane; aminopropyl; nonaqueous titration; size exclusion chromatography; nuclear magnetic resonance

INTRODUCTION

In recent years materials scientists in the marine biological fouling release field have been pursuing materials that are both tough and soft.^{1–5} The need for this seeming contradiction in properties comes about because of the harshness of the physical forces on hull coatings in the ocean and dockside and the theory that an interface between a soft, amorphous coating and seawater provides for weaker attachment of organisms than an interface between a hard and/or crystalline solid and seawater.⁶ A telechelic fluorinated siloxane with reactive nonfluorine end groups might be a good choice for one component of such a material because the flexible siloxane linkage allows low surface energy groups to be oriented away from the polymer bulk, at least in an air cure. The polar end groups or the functionalities formed from the reaction of them could form hydrogen

bonded regions to potentially serve as crosslinking and thus strengthening sites. Oligo(dimethylsiloxane)s with aminopropyl end groups have been studied,^{7–10} but bis(aminopropyl) oligomers containing methyl trifluoropropyl siloxane instead of the dimethylsiloxane moiety have yet to be fully established. Reported here are the synthetic efforts toward this end and characterization via IR, end group titration, size exclusion chromatography, NMR, and enhancement of the end group NMR signal for molecular weight purposes by reaction of the end groups with an appropriate capping molecule.

EXPERIMENTAL

Trimethyltris(trifluoropropyl)cyclotrisiloxane (TFP), the cyclic trimer of $\text{H}_3\text{CSiO}(\text{CH}_2\text{CH}_2\text{CF}_3)$, was obtained from PCR, Inc. (Gainesville, FL). Bis(aminopropyl)tetramethyldisiloxane (AP), formula $[\text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2(\text{CH}_3)_2\text{Si}]_2\text{O}$, was from Hüls. Tetrahydrofuran (THF), chloroform-*d*, 1.0M diethylzinc in hexanes, +99% picric acid containing 35% H_2O , 2-propanol, and the sodium

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salt of bromocresol green were purchased from Aldrich Chemical. THF- d_8 was obtained from Cambridge Isotopes (Woburn, MA).

A Bruker AC 250 spectrometer was used for ^1H -NMR spectra obtained in THF- d_8 , which were calibrated relative to residual THF- d_7 at $\delta = 3.58$ ppm. Proton NMR spectra of samples in chloroform- d were collected on a Bruker DPX 300. All ^{13}C , ^{29}Si , and ^{19}F spectra were obtained in chloroform- d on the Bruker DPX 300. Chemical shifts for ^1H in chloroform- d were relative to internal tetramethylsilane (TMS, 0.00 ppm). Chemical shifts for ^{13}C were set relative to internal TMS (0.00 ppm) or the chloroform- d triplet (77.0 ppm), and a composite pulse decoupling sequence was used for ^1H decoupling.¹¹ Chemical shifts for ^{19}F were relative to internal $\text{CF}^{35}\text{Cl}_2$ ^{37}Cl (0.00 ppm), and an inverse gating program was used for ^1H decoupling. Proton decoupled ^{29}Si spectra were referenced to internal TMS (0.00 ppm) and obtained with a relaxation delay of 17 s using inverse gated decoupling to eliminate the negative nuclear Overhauser effect. The IR spectra were obtained on NaCl plates on a Perkin–Elmer 1310 instrument. Size exclusion chromatography was done in THF on two Altex μ -spherogel columns (10^2 and 10^3 nm) connected in series with a Wyatt/Optilab 903 refractive index detector and polystyrene standards. The number- and weight-average molecular weights (M_n and M_w) were determined using a program written by Dr. T. Ho. Nonaqueous end group titrations were performed by the addition of picric acid in 2-propanol to a solution of the siloxane, the sodium salt of bromocresol green, and THF. Diethylzinc was transferred in a Vacuum Atmospheres Corporation glove box filled with N_2 .

Materials **1**, **2**, and **3** were made with target molecular weights of 4940, 7700, and 26100 g/mol, respectively. The target molecular weights are based on an assumed perfectly monodisperse α,ω -di(aminopropyl) siloxane with 100% conversion of AP and TFP and an $\text{H}_3\text{CSiO}(\text{CH}_2\text{CH}_2\text{CF}_3)$ polysiloxane backbone repeating unit. A representative preparation (oligomer **2**) follows. A mixture of 5.3375 g (0.011392 mol) of TFP and 0.1779 g (0.0007158 mol) of AP in a flask with a stirring bar and stopcock were placed under a dynamic vacuum for 3 h. The stopcock was closed and the apparatus was transferred to the glove box. A Pasteur pipet was used to transfer about 0.01 mL of 1.0M diethylzinc in hexanes, which contained about 1×10^{-5} mol of diethylzinc, to the flask. The sealed reaction mixture was heated at 80°C

outside the glove box under N_2 with stirring for 48 h. The mixture was exposed to air during the setup of the distillation apparatus. Vacuum distillation was then done for 3 h at 80°C, and no material was distilled; both starting materials (AP and TFP) can be distilled under these conditions. The oligomer obtained was colorless and highly viscous.

RESULTS AND DISCUSSION

TFP reacts with AP and a substoichiometric amount of the initiator diethylzinc to give fluorinated siloxane oligomer amines **1–3**. The characterization of these three oligomers is presented after some discussion of one of the starting materials.

TFP as received from the manufacturer is typically a colorless viscous liquid over a soft white solid. A separation was done to better understand what these two phases contained. The separation entailed a filtration at 25°C, giving solid TFP. The filtrate from the room temperature filtration was cooled to 0°C and filtered. The filtrate from the 0°C filtration was cooled to -78°C and filtered. The filtrate from the -78°C filtration was designated liquid TFP, from which some spectra were obtained at ambient temperature.

NMR data on TFP using ^1H , ^{13}C , ^{29}Si , and ^{19}F as the observed nuclei are presented in this article. There are no previously reported TFP ^{13}C and ^{29}Si spectra, but there are spectra for the other two nuclei. The reports include a chloroform- d and acetone- d_6 ^1H study¹² and a CCl_4 and acetone- d_6 ^1H and ^{19}F study.¹³ The ^1H decoupled ^{13}C -NMR of solid TFP is given in Figure 1, where the prominent quartet structure is due to coupling between ^{13}C and ^{19}F . Expansion of the CF_3 quartet at 128 ppm reveals two quartets expected for the trans isomer, and two CF_3 groups are on one side of the ring and one is on the opposite side. Liquid TFP exhibits three quartets in this region, indicating that it contains both cis and trans isomers, a conclusion generally supported by the other nuclei. Thus, solid TFP collected at room temperature is trans and liquid TFP isolated at low temperatures is a solution of trans and cis, which agrees with melting points of 35.2°C for the trans isomer and 15.5°C for the cis.¹⁴ Complete ^{13}C data are presented in Table I. Assignments in this table are based in part on the relative intensities of the signals in the trans sample. Multiple ^{13}C spectra were obtained on

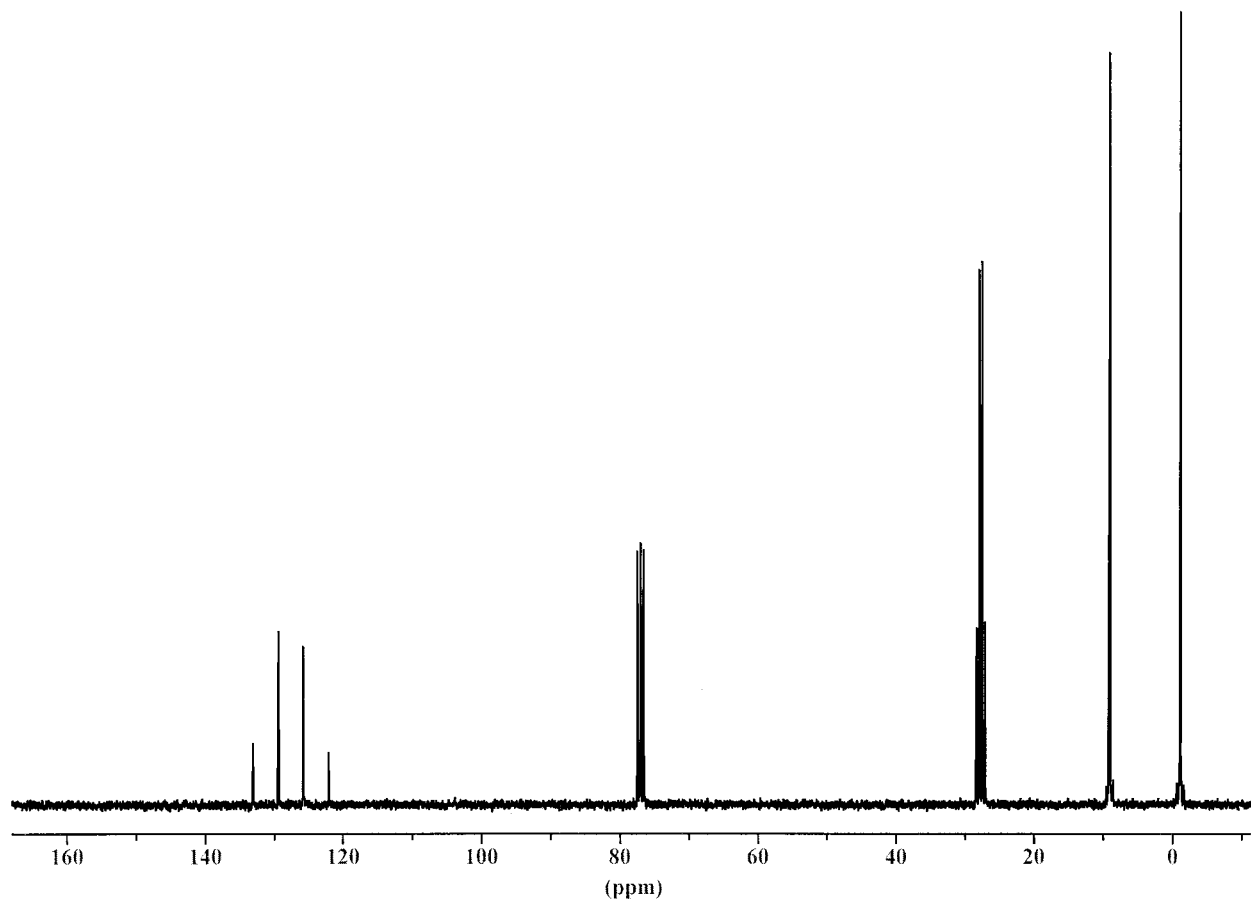


Figure 1 The ^1H decoupled ^{13}C -NMR of solid TFP in chloroform-*d*. The regions from left to right are CF_3 , solvent, methylene carbon of CF_3CH_2 , CH_2Si , and CH_3Si .

liquid TFP from different isolations, and the ratio of *trans*- to *cis*-TFP varied in these samples. As a result, assignments were also based on the simultaneous rise of sets of peaks with the concentrations in samples containing both *trans*- and *cis*-TFP, relative to other peaks (from the other stereoisomer).

The ^1H decoupled ^{29}Si spectra of various TFP samples in chloroform-*d* exhibited one singlet instead of the two expected for a *trans* sample and the three expected for a *trans* + *cis* sample. The singlet appeared at -9.64 to -9.74 ppm in a sampling of five spectra. The spectra were free from extraneous peaks from $+326.71$ to -191.30 ppm, except for a broad peak centered at -114 ppm, which was due to glass in the tube and probe. In an effort to increase the resolution, a spectrum of solid TFP was collected with more data points and a lower spectral width; only one peak was seen. Apparently the environments provided by *cis* and *trans* alkyls were not different

enough for a detectable chemical shift difference. One unfiltered sample containing both *cis* and *trans* TFP showed a peak in the baseline at -22.40 ppm. The other spectra were flat in this region. The difference between the chemical shift of this peak and that of the -9.6 peak suggests that it may have been due to the less strained cyclic tetramer. The analogous situation in cyclic dimethylsiloxanes showed a cyclic trimer at -9.5 ppm and a cyclic tetramer at -19.8 .² The ^{29}Si chemical shift of a noncyclic and unstrained nonafluoro polymer containing the same ethylene spacer as TFP, $-(\text{H}_3\text{C})\text{Si}[\text{CH}_2\text{CH}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_3]\text{O}-$, was -21.6 ppm.^{15,16} As an independent verification of the comparability of chemical shifts in the present work and the literature, the cyclic dimethylsiloxane tetramer was examined. The shift was -19.21 ppm, essentially in agreement with the published value.² Thus, although the ^{29}Si spectra of TFP exhibited only one peak, it appears they revealed the absence of the less strained

Table I ^{13}C -NMR Chemical Shifts (ppm), Multiplicity, and Coupling Constants (J_{CF} , Hz) of *trans*- and *cis*-TFP

TFP Isomer	Carbon	Chemical Shift	Multiplicity	J_{CF}
<i>trans</i>	2 <i>cis</i> -CH ₃ ^a	-1.15	s	None
<i>trans</i>	2 <i>cis</i> -SiCH ₂ ^b	9.0-9.2	m	~2
<i>trans</i>	2 <i>cis</i> -CH ₂ CF ₃ ^c	27.72	q	30.8
<i>trans</i>	2 <i>cis</i> -CF ₃ ^d	127.60	q	276.0
<i>trans</i>	<i>trans</i> -CH ₃ ^e	-1.19	s, shoulder	None
<i>trans</i>	<i>trans</i> -SiCH ₂ ^f	9.0-9.2	m	~2
<i>trans</i>	<i>trans</i> -CH ₂ CF ₃ ^g	27.72	q	30.8
<i>trans</i>	<i>trans</i> -CF ₃ ^h	127.66	q	276.0
<i>cis</i>	CH ₃	-1.38	s	None
<i>cis</i>	SiCH ₂	9.0-9.2	m	~2
<i>cis</i>	CH ₂ CF ₃	27.72	q	30.8
<i>cis</i>	CF ₃	127.80	q	275.7

s, singlet; q, quartet; m, multiplet.

^a Two methyls that are *cis* to each other.

^b Two SiCH₂ groups that are *cis* to each other.

^c Two CH₂ groups in CH₂CF₃ groups that are *cis* to each other.

^d Two trifluoromethyls that are *cis* to each other.

^e The methyl that is *trans* to 2 *cis*-CH₃.

^f The SiCH₂ that is *trans* to two SiCH₂ groups that are *cis* to each other.

^g The CH₂ in CH₂CF₃ that is *trans* to two CH₂ groups in CH₂CF₃ groups that are *cis* to each other.

^h The trifluoromethyl that is *trans* to two trifluoromethyls that are *cis* to each other.

cyclic tetramer in our filtered samples. The manufacturer indicates that the TFP as supplied is 99% cyclic trimer and 0-1% cyclic tetramer.¹⁷

The ^{19}F results were in general agreement with the literature.¹³ They showed very clearly that the *trans* isomer is the only component of solid TFP and that liquid TFP contains the *cis* and *trans* stereoisomers in varying amounts, depending on the filtration.

The IR spectra of oligomers **1-3** gave the expected C—F stretching bands near 1250 cm⁻¹ and Si—O—Si stretching modes near 1050 cm⁻¹. There was a variation in the intensity of the NH stretching at 3350 cm⁻¹ in the order AP > **1** > **2** \cong **3** > TFP, as expected. This region was almost flat in the two oligomers with the highest molecular weight.

The M_n of the oligomers was determined by nonaqueous titration. Siloxanes are fairly hydrophobic and attempts at colorimetric and potentiometric titrations in partially aqueous solutions resulted in two clearly visible phases, which introduces questions about whether all of the amines are protonated. The nonaqueous titration was based on previously published methodology¹⁸ and proceeded without formation of a second phase. A 2-propanol solution of picric acid was prepared by dissolving solid picric acid. Although

this introduced the water of stabilization in the picric acid, the amount was very small because the amount of acid needed for this end group analysis was also very small. The solution was standardized with aqueous NaOH, yielding a picric acid concentration of 4.83×10^{-3} mol/L. The oligomeric amine was dissolved in THF and a few drops of a 7×10^{-5} mol/L solution of the sodium salt of bromocresol green in 2-propanol were added, which produced a blue solution. Titration with the standard picric acid solution gave a single phase all the way to, and including, the end point. The results were: AP, 270 g/mol; **1**, 9500 g/mol; **2**, 17,000 g/mol; and **3**, 61,000 g/mol. The molecular weight of AP calculated from its formula is 249 g/mol, which shows that the method gave one result that was 8.4% high.

To provide another estimate of the M_n , the end groups of oligomeric amine **1** were amplified by a reaction with *tert*-butyl isocyanate, giving a urea linkage and an end group 9/2 as intense for ^1H -NMR purposes. Comparison of the THF- d_8 ^1H spectra of AP, TFP, *tert*-butyl isocyanate, and the *tert*-butyl isocyanate adduct of **1** aided in the assignments. In the adduct, the areas of the *tert*-butyl singlet (the end group) and the CF₃CH₂ methylene (the central portion of the polymer)

gave a number-average molecular weight for **1** of 8000 g/mol, assuming a diamino oligomer. When AP was subjected to the same procedure, this procedure gave an AP molecular weight of 231 g/mol, which is 7.2% lower than the true molecular weight of 249. Aside from providing another M_n method, the $^1\text{H-NMR}$ spectra give evidence that **1**, **2**, and **3** were almost free of AP or TFP starting materials. AP had a methyl singlet at 0.05 ppm and TFP had an intense singlet at 0.25. The spectra of **1–3** exhibited a small peak at 0.05 ppm and a small shoulder at 0.25 ppm.

The titration-derived and NMR-derived M_n values above are clearly much higher than the target molecular weights. This may be due to evaporation of some of the starting material, in particular the amine (AP), in the preparative evacuation step.

Size exclusion chromatography of **3** showed a monomodal oligomer peak with $M_n = 49,000$ g/mol and $M_w = 72,000$ g/mol, based on polystyrene standards, and a small peak corresponding to TFP. The lower molecular weight oligomers **1** and **2**, on the other hand, gave poorly defined polymer peaks and prominent TFP regions. These systems may be prone to redistribution, but the results were still surprising considering little TFP was seen in the $^1\text{H-NMR}$ spectra of all three materials in THF- d_8 and essentially the same solvent, THF, was used as the size exclusion chromatography solvent.

To provide some understanding of the reaction mechanism, the following data were collected. TFP and the diethylzinc initiator (without AP) was stirred at 80°C for 25 h. White needles were obtained as the reaction product. Size exclusion chromatography showed only TFP, and the $^1\text{H-NMR}$ in THF- d_8 was identical to that of TFP. If both ethyl groups in an anionic ring-opening reaction initiated chains and all chains were of equal length, the projected molecular weight would be 53,000 g/mol, which was removed by hundreds of seconds from TFP in the size exclusion chromatography trace. Thus, it appears that diethylzinc does not attack TFP in the course of this reaction.

CONCLUSION

The oligomeric fluorinated siloxane amines formed are probably difunctional (i.e., siloxane diamines). The products at the end of the reactions, which were done in the absence of solvent,

remained highly viscous in the continued absence of solvent. However, this system may be prone to redistribution, particularly in the presence of a cyclic ether solvent such as THF. The nonaqueous titration of the amine functionality described in this article requires simple equipment and little time, is moderately accurate, and proceeds with the complete absence of two phase formation in these oligomers that contain large weight percentages of groups traditionally leading to insolubility in H_2O (fluorocarbons and alkyl siloxanes). The amplification of the amine end groups for $^1\text{H-NMR}$ analysis is straightforward and also moderately accurate, based on a material of known molecular weight, and allows extension of number-average molecular weights to higher values.

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